Supporting information

METHODS

Preparation of BNNTs

The BNNTs were synthesized by a chemical vapor deposition method using boron and metal oxides as precursors. The detailed growth procedure was reported elsewhere [1]. The as-grown BNNTs were purified at ~ 1900 ^{o}C under the protection of Ar to remove impurities. Purified BNNTs were "snow-white" in color. The BNNTs were put in an alumina crucible and oxidized at 1000 ^{o}C for 5 hours. The oxidized BNNTs were placed into a bottle with enough amount of water and ultrasonically dispersed for 5 h. Then they were filtered off after sonication and re-suspended in water at 25 μg/mL concentration.

Preparation of BNNTs@$NaGdF_4$:5mol%Eu structure

The $Gd(OH)CO_3 \cdot H_2O$: Eu layer was first synthesized in the presence of BNNTs by a homogeneous precipitation method. In a typical synthesis, 80mL of BNNTs suspensions were sonicated for 2 h. Then, 0.054g of urea were added and sonicated for another 2 h. As control, 0.027g and 1.08g of urea were also used to get the final products at too low and too high concentration of urea. Afterward, certain amounts of 1.0 M $GdCl_3$ (Low-104.5μL, High-209μL) and 0.05 M $EuCl_3 \cdot 6H_2O$ were added to the above BNNTs suspensions with urea. The mixture was sealed in a glass bottle and heated to 90 °C for 2 h or 2.5 h. The resulting dispersions were centrifuged at 10000 rpm for 10 min, the supernatant solution was discarded, and the particles were re-suspended in ethanol with an ultrasonic bath. This process was repeated 3 times and the precursor was dried and stored in a desiccator. BNNTs@Gd_2O_3: Eu was obtained by thermal treatment of the precursor at 700 °C for 8 h (2 °C/min to 700 °C), the morphology was retained after the heat treatment. Then, BNNTs@Gd_2O_3: Eu prepared as the above was reacted with NaF and HF aqueous solution at 80 °C for 2 h to convert into BNNTs@$NaGdF_4$: Eu. After cooling, the powder sample was washed with deionized water and ethanol for several times, and dried at in a desiccator overnight.

Characterization

The morphology and structure observations were carried out by using a JEM-3000F transmission electron microscopy (TEM) operated at 300 kV. Ultraviolet–visible (UV-vis) spectroscopy was used to record the dox concentration before and after loading. The room temperature photoluminescence (PL) spectra were measured by micro PL system (λ=325nm, LabRamHR-PL). The differential interference contrast (DIC) and confocal fluorescence images for BN@$NaGdF_4$:Eu composites uptaken by LNcap prostate cancer cells were acquired by an SP5 confocal fluorescence microscope (CLSM; Leica microsystems, Germany). Isothermal magnetization measurements were performed on a SQUID magnetometer (Quantum Design, MPMS) between -70 and 70 kOe at 300 K.

LNcap prostate cancerous cell culture with BNNTs@$NaGdF_4$:Eu composites

LNcap prostate cancerous cells with a cell density about 6×10^4 cells/cm^2 were cultured in 48-well plates containing RPMI1640 medium supplemented with 10% fetal bovine serum (FBS), 100 units/mL penicillin, and 100 mg/mL streptomycin at 37 °C in humidified air containing 5% CO_2. After 1 day, BNNTs@$NaGdF_4$:Eu composites were added into the above wells at a final concentration of 2.5, 5, 10 and 20 μg/ml, respectively. The uptaken experiments were performed in the absence and presence of a magnetic field (Neodymium Iron Boron magnet, φ1*0.6 cm, 7517 Gauss) applied beneath the culture plate. After 3 h of incubation, the cells were carefully washed twice with PBS. The internalized BNNTs@$NaGdF_4$:Eu was quantified fluorometrically (λ_{ex}=380 nm, λ_{ex}=610 nm).

Loading dox onto BNNTs@$NaGdF_4$:Eu composites

1 ml of BNNTs@$NaGdF_4$:Eu suspensions at 50 μg/ml in PBS solution (pH=8.0) and 50 μl of dox solution at 1 mg/ml in water were mixed and shaken at 800 rpm for about 16 h at room temperature. Then, the mixture was repeatedly filtered through a 10kDa membrane, and washed to remove free dox until the supernatant became nearly colorless.

LNcap prostate cancerous cell culture with dox-loaded BNNTs@$NaGdF_4$:Eu composites

LNcap prostate cancerous cells with a cell density about 6×10^4 cells/cm^2 were cultured in 48-well plates containing RPMI1640 medium supplemented with 10% fetal bovine serum (FBS), 100 units/mL penicillin, and 100 mg/mL streptomycin at 37 °C in humidified air containing 5% CO_2. After 1 day, BNNTs@$NaGdF_4$:Eu composites were added into the above wells at a final concentration of 0.2, 0.5, 1, 2, 5 and 10 μg/ml, respectively. The experiments were performed in the absence and presence of a magnetic field (Neodymium Iron Boron magnet, φ1*0.6 cm, 7517 Gauss) applied beneath the culture plate. After incubation for 3 h, the culture medium in all wells was changed with fresh medium. After another 24 h incubation, the LNcap prostate cancerous cells viability were checked using a CCK-8 kit (Dojindo Molecular Technologies, Japan) in accordance with the manufacturer's instructions.

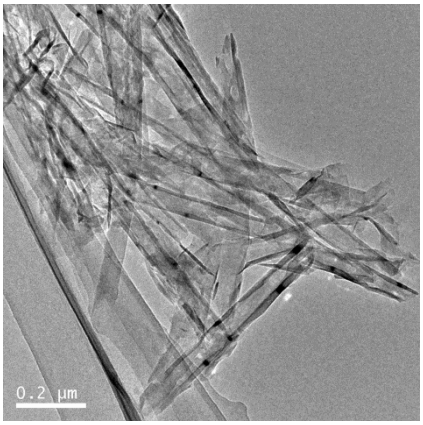

Fig. S1 TEM image of BNNTs.

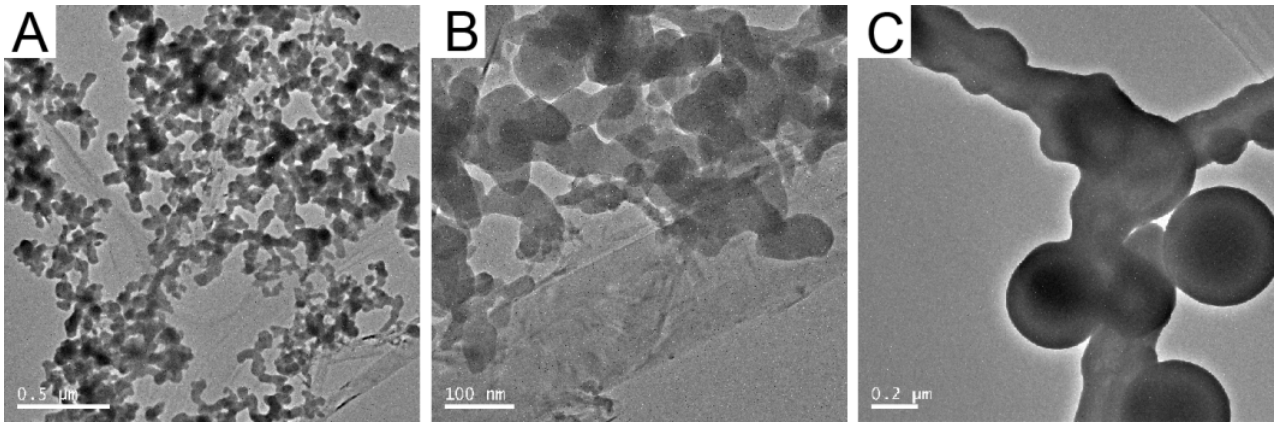

Fig. S2 TEM images of BNNTs@Gd(OH)$CO_3 \cdot H_2O$: Eu composites synthesized at too low urea concentrations (A, B) and at too high urea concentrations (C).

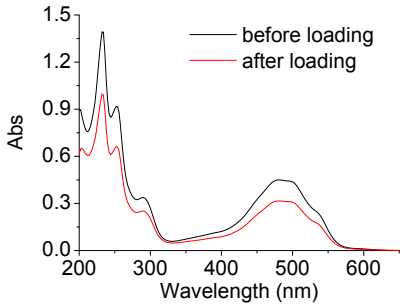

Fig. S3 UV-vis spectrum of the dox solutions before and after loading onto a BNNTs@NaGdF4: Eu composite.

References.

(1)Tang, C.; Bando, Y.; Sato, T.; Kurashima, K. Chem Commun 2002, 1290.